

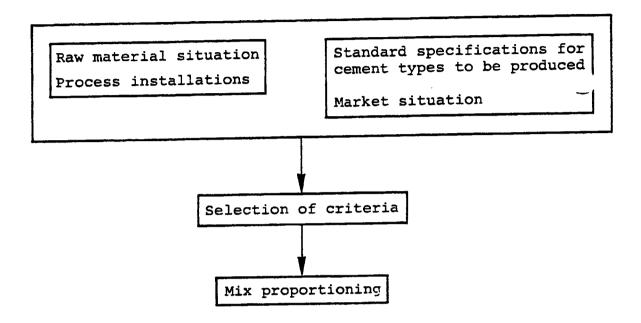
MIX DESIGN

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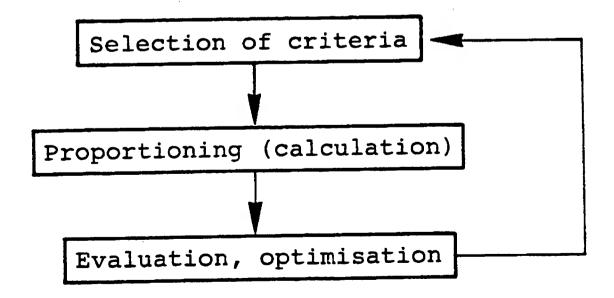
1. GENERAL

A raw mix design comprises not only raw mix proportioning but also considerations of such factors as standard specifications of the cement types to be produced, the market situation and the available process installations.



The selection of criteria is dictated by the standard specifications.

Designing raw mixes does not only involve the proportioning (calculation) but includes an evaluation of the obtained results. The latter involves optimisation with respect to costs and materials.

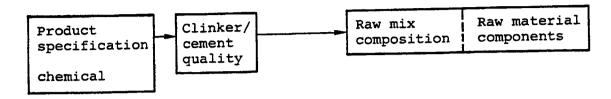




2. DEFINITION OF CRITERIA FOR MIX CALCULATION

Any type of cement has to conform to the individual cement standards of a particular country. Standards (standard specifications) normally include chemical specifications for clinker and cement. Together with the physical and strength requirements, they guarantee a suitable quality potential for the respective cement type.

With regard to the raw material aspects only the chemical requirements are significant:



In other words: the product specifications dictate the clinker/cement quality which in turn dictates the chemical composition of the raw mix and finally the selection of the raw material components.

The above sequence can also be reversed: an existing raw material configuration with little freedom as to the proportioning of the raw mix, may permit the manufacture of only one particular type of clinker.

Table 41 Influence of chemical requirements on raw materials

Chemical requirements	Influence on raw material
min. SO ₃	Rejection of SO ₃ -bearing components (e.g.) gypsum-containing shale)
min. MgO	Rejection of MgO-bearing components (e.g. dolomitic limestone)
min. Alkali	Selection of raw material with low alkali-content
min. C ₃ A	Selection of components with very low alumina content and / or high iron content

Table 41 shows the influence of chemical requirements on the choice of raw materials.

The following chemical criteria are normally used as a basis for raw mix proportioning (Table 42; on clinker basis):

Table 42 Chemical criteria for raw mix proportioning

criteria	"normal" range limit	formulas, remarks
	(for clinker)	
MgO	max. 5% (6%)	for all cements
so ₃ *	3 - 4,5%	depending on cement type
LIME STANDARD OF LIME SATURATION FACTOR	0,9 - 1 or 90 - 100%	CaO 2,8 SiO ₂ + 1,2 Al ₂ O ₃ + 0,65 Fe ₂ O ₃
"Improved" Lime standard **	90 - 100%	100 (CaO + 0,75 MgO) ** 2,80 SiO ₂ + 1,18 Al ₂ O ₃ + 0,65 Fe ₂ O ₃
Index of activity Hydraulic ratio	2,5 - 3,5 2,0 - 2,4	$\frac{\sin_2}{\frac{\sin_2}{\text{Al}_2\circ_3}}$ $\frac{\cos_2}{\text{Al}_2\circ_3}$ $\frac{\cos_2}{\text{Al}_2\circ_3}$ $\frac{\cos_2}{\sin_2 + \text{Al}_2\circ_3 + \text{Fe}_2\circ_3}$
SILICA RATIO	1,8 - 3,4	SiO ₂ Al ₂ O ₃ + Fe ₂ O ₃
ALUMINA RATIO	1,5 - 2,5 (0,7 - 3,5)	Al ₂ O ₃ Fe ₂ O ₃
Total alkali	< 0,6%	Na ₂ O + 0,66 K ₂ O for low alkali clinker
c ₃ s	50 - 60%	except for ASTM type IV
C ₃ A	max. 3% BS max. 5% ASTM	for sulfate-resisting cement

^{*} for cement

The proportioning of raw mixes for ordinary Portland cement is mostly based on the following specific criteria:

- ♦ MgO
- Lime standard or lime or saturation factor (or C₃S)
- Silica ratio
- Alumina ratio

^{** 100 (}CaO + 1,5) for MgO<2%



As Table 42 indicates, ratios are the preferred chemical criteria for proportioning since they offer the advantage of expressing the main and most important chemical parameters such as SiO₂, Al₂O₃, Fe₂O₃ and CaO in one single figure.

Other important criteria such as type and composition of fuels should not be overlooked. Coal ash as a combustion product of coal, for instance, has to be analysed quantitatively and qualitatively and should be treated as an individual raw material component. Fuel oil has to be considered as a potential carrier of sulphur, etc.

Additional criteria which could have bearing on the mix proportioning refer to <u>performance</u> characteristics, e.g.:

- minimum dust emission
- burnability and coating properties
- extreme components which affect machine performance

or to economic factors, e.g.:

- maximum overall economy
- easy and simple operations
- minimum number of components

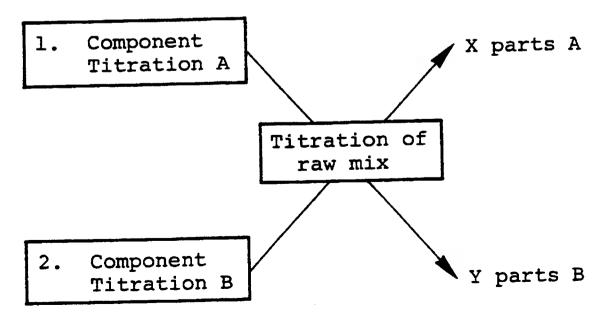
However, performance characteristics in particular can normally be controlled regarding the "normal" chemical requirements for cement raw mixes. The economic factors, on the other hand, are of the same significance as the chemical requirements.

3. PRINCIPLES AND METHODS OF MIX PROPORTIONING

Proportioning (calculation) of potential cement raw mixes can be accomplished by various methods:

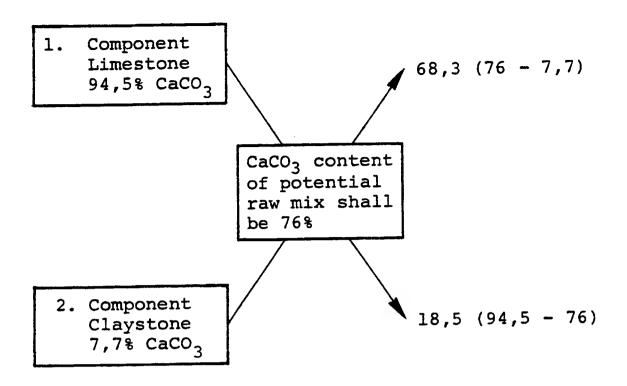
3.1 X-Pattern

The x-pattern represents a linear estimation of two raw material components by selecting the anticipated titration value (total carbonate content) of the potential raw mix as basis.



or as a numerical example.





The potential raw mix with a titration value of 76% would thus consist of:

$$\frac{\text{limestone}}{\text{claystone}} = \frac{68.3}{18.5} = \frac{3.69}{1}$$

or

limestone 78,6 % claystone 21,3 %

The resulting analysis of the raw mix has to be checked with regard to the requirements of the standard specifications.

3.2 Manual Calculation

There are a number of mathematical methods for two and three-component systems. Formulas are not complicated but comprise a large number of steps. The method of manual calculation as such is outdated.

3.3 Graphical Methods

These methods require preparatory work (manual calculations) for the determination of the relevant figures which are the basis for the construction of the diagrams and graphs. Graphical methods represent a rather archaic stage of mix proportioning.

3.4 Programmable Calculator

Programmable calculators normally produce one solution (out of possibly several). Obviously, this method is the best way to obtain a quick solution.

3.5 Computer Optimisation

It provides the optimum of a series of possible solutions considering the price factors as variables. If the available raw materials cannot meet the specified requirements for the raw

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mix, an approximate and an exact_solution considering the missing constituents are produced (Tables 43 - 47).

Note: Mix calculations are normally based on dry raw materials. In practice, the natural moisture contents of the raw material components have to be considered too. This may entail alterations of the original mix proportions.

Table 43

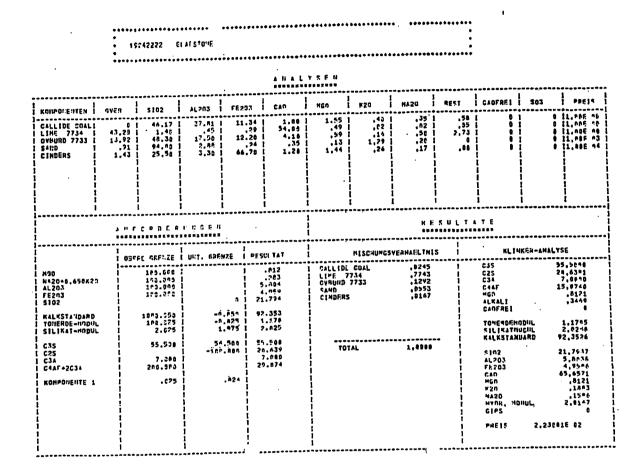




Table 44

2064 05050-0	44 MIXES ILI				28. 6. 77 (PTIMIERUNG
		ANALYS	EN			
NR GVER SIG2	AL203 FE203	CAO MGO K20) NA20 TIO	CRO MNO SO	3 P20 CL F	REST PREIS
1 4290 190 2 1925 4150 3 839 6380 4 293 1477 A N F O R D	1207 599 1 1329 400	576 ·239 99 340 92 219 247 53 40	109 52 250 44	0 9 8 0 8 9 0 6 9 0 2 141 TATE	11 9 (8 11 (45 . 10+00 0 . 10+00 0 68 . 22+00 0 65 . 59+00
	max. MIN	. RRESULT	rat misch	UNGSVERHAEL	TNIS KLINK	ERANALYSE
MGO NA20+, 659K2O AL203 FE203 S102 KALKSTANDARD TONERDEMODUL S1LIKATMUDUL C2S C2S C3A C4AF+2C3A KCMPON, 1	100,000 100,000 100,000 100,000 1000,050 1 2,595 20,500 59 100,000-100 200,000-100	. 000 9. 669 . 000 23. 521 . 000 . 753	LIMESTON SHALE LO SHALE HI PYRITE C	H .1262 GH .1145 IND .0059 .0000 .0000 .0000 .0000 .0000 .0000	C2S C3A C4AF MG0 ALMALI HYDR. MODI TUNERDEMI SILIMATMI KALKSTANI S102 AL203 FE203 CAO MG0	DUL 1. 8450



Table 45

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7852 BIRSO,644 MINES ILIGIM NO. 1

	EN 1 5102	AL203 7	 E20j	ĊA0	нао	X20	MAZO	REST	CADPRET	\$03	 P4E15
LIMESTONE . ! 4 SHALE LOW ! ! SHALE MIGH ! PYRITE CIND!	7,90 1,98 9,30 41,48 8,49 63,48 2,96 14,9 3,50 89,36	.07 1 12.10 1 13.36 1 2.90	.48 6.86 4.81 73.68 2.58	52,94 15,86 1 3,46 1 2,58	2,41 93 59	1,00 2,20	1,19 2,50 ,32	1 1,47			11,40E 41 11,40E 41 12,10F 01 13,41F 91 13,65E 41 1
	1 N T C R D E] 	HIZCHUHES	*******	S U L 7 4		(ER-AMALT	 IE
M90 M120-6,698K20 M1203 FE203 S108	OGERE GREAT	1	,	.251 .432 .444 .809 .821	I LIMEST SWALE SWALE PYRITE SILICA	CIND HIGH OME	,7472 ,1912 ,0121 ,8121	1	CJS CJS CJA C4FF HGO ALRALI CAOFREI	1	8,5078 8,7992 5,9272 1,5783 1,2518 ,7575
KALKSTANDIAD TOMERCE-MODUL SILIKAT-MODUL C3S C3A C4AF+2C3A	1 100.05 1 .22 2,42 1 68.50 1 100.00	1 1.17 2.97 1 47.58 1 -107.58	5 1 5 6 6 3 6 3	1,437 1,225 1,575 1,588 1,089 1,089	701		\$,0 0 00	! ! ! !	TOMERBEND SILIKATHO MALKSTAND FERDD CAO PAO PAO PAO PAO PAO PAO PAO PAO PAO P	100 100 2	1,2250 2,5798 6,4373 1,8212 4,6656 3,8097 8,6193 1,2510
ROMPOVENTE 1	1.00 1 1 1	 					(#20 #20 #420 #400 #400 #400 #400		,3545 ,3978 2,1005



Table 46

OPTIMALISIERUNG

2057 B5850,844 MIXES ILIGAN NO, 7

				*****	ANAL	7 S E H						·•••••
COMPONENTER !	CVEÁ	5102	AL203 F	£203	ČA0	MG0	K50	PSAN	REST	CAOFREI	503	PRE
LIMESTONE : SHALE LOW : SHALE HIGH : PYRITE GIND: SILICA SAND:	42,90 19.33 8,40 2,96 3,50	41,48 83,88 14,90	2.90 13.30 12.10	.40 6.56 4.60 73.60 2.18	15,80 3,40 2,50	93	1,88 2,20 41	1,10 2,50 3,32	1,47 1,82		1	11.00F 12.10E 12.10E 15.05E 1
		C R D E P	UN O E Y	I RES	ULTAT			YERHAELTHI		#LINKE	 P-1881-8	:E
160 1420-9,658K20 14203 15203 1702	1		8] 5] 5] 2i	,488 .821 .874 .718 .593	LIMESTO SHALE L SHALE P PYRITE SILICA	NE ON Ilgh CIND	,7163 ,2005 6 ,0020 ,0152	:	CJS C2S C3A C4AF HGD ALKAL! CADFRE!	17	,5050 ,8454 ,1259 ,7839 ,4877 ,9789
TALKSTANDARD TONERDE-MODUL TILIKAT-MODUL TS TS TALKSTANDARD TS		1000.050 1.825 2.425 60.500 100.000 200.000	1 1,775 2,375 1 59,500 1 -300,000	5 1 1.825 5 1 2.375 1 50.500		TOTA		1,0000	- 1	TOMERDEMODI SILIKATHODI KALKSTANDAR SIOZ ALZOS FEZOJ	2	2 1,8250 1,3758 1,6540 1,6540 1,6736 1,8736
OMPONENTE 1	; ; ; ;	1.000	۵	1		 			I I I I	CAO MGO K2O MA2O MYOR, MODUL GIPS	•	3,7698 ,4877 ,4625 ,5164 2,1434



Table	47
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2011	OSOSO=044	MITES	ILIGAN	ML	77	ı

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ANALYSEN

	P1 17		
NR GVER \$102	AL203 FE203 CA0	MGO K20 NA20 TIO CRO MN	O SO3 P20 CL F REST PREIS
1 4290 190 2 1925 4150 3 639 6380 4 293 1477	69 39 5290 1207 598 1576 1329 400 340 287 7297 247	42 4 4 3 0 8 239 99 109 52 0 8 92 219 250 44 0 6 53 40 31 55 0 2	9 11 9 0 0 . 10+00
ANFORD	ERUNGEN	RESULTAT	Ε
	MAX. MIN.	RRESULTAT HISCHUNGSVER	HAELTNIS KLINKERANALYSE
MGO NA20+. 659K2O AL203 FE203 SIO2 KALKSTANDARD TONERDEMODUL SILIKATMODUL C3S C2S	100, 000	1. 010 SHALE LOW 5. 933 SHALE HIGH 3. 216 PYRITE CIND 21. 453 94. 860 1. 845 2. 345 59. 500 16. 642	7290 C3S

OPTIMUM PREIS .11111+00

MGO 1. 3622 K20 . 5672 NA20 . 6369 T102 . 2507 CR203 . 0000 MN203 . 1259 S03 . 1410 P205 . 0927 CL . 0538 F . 0000

REST

. 57699

4. PRINCIPLES OF RAW MIX ASSESSMENT

Basically, evaluation and assessment of raw material components (4.4) and raw mixes refer to the same principles. The only difference exists in the immediate comparison of the chemical composition of a raw mix with the <u>standard specifications</u> of the products for which it is intended.



4.1 Mix Type

The possible combinations of different rocks used in raw mixes can be classified as mix types. Important varieties are:

- Argillaceous limestone (marl) having the composition of a natural cement. An optimum homogenisation is realised in the rack texture itself. The reactions can easily take place even with a coarsely grained raw mix.
- ◆ The same rock in a metamorphic condition contains well crystallised silicates instead of clay minerals. Under otherwise similar conditions, the reactivity is lower than in the first case and there is a high probability that dust formation will occur in the preparation and burning process.
- ◆ Contrary to the above cases is the combination of pure limestone with pure clay. To get a close contact between lime and silicate, both components have to be ground finely and homogenised intensively. Depending on the type of clay minerals, the mixes can be more or less reactive,
- ◆ A further mix type is the combination of relatively pure limestone, argillaceous limestone and sandstone. Quartz introduced by the sandstone will decrease the grindability and the burnability to some extent. Problems may occur when less reactive minerals are present in the other two components.

Rock combinations actually used can easily be related to this series of mix types. The situation becomes more complicated when additions like pyrite ash, iron ore or bauxite are used.

4.2 Comparison of Raw Mix with Standard Specifications

Any raw mix composition has to be compared with the locally applied standard specifications in order to evaluate potential conformity. As an example, Table 48 compares two analyses of typical Portland cements with the ASTM-specifications for the five main types of Portland cement, whereby these types are designated as follows:

Type I	Ordinary Portland cement			
Type II	Moderate sulphate resistance or moderate heat of hydration			
Type III	High early strength			
Type IV	Low heat of hydration			
Type V	High sulphate resistance			

Table 48 Raw mix composition and specification.

		nker osition	d		quirements a		0
	Ï	II	ı	II	111	IV	V
Loss on ignition	0.43	0.69	<3.0	<3.0	<3.0	<2.5	<3.0
SiO ₂	20.8	22.8		>21.0			
Al ₂ O ₃	6.0	3.8		<6.0			
Fe ₂ O ₃	2.5	4.4		<6.0			:
CaO	66.7	65.2					
MgO	1.4	2.2	<6.0	<6.0	<6.0	<6.0	<6.0
So ₃ *	0.52	0.16	<3.0 <3.5	<3.0	<3.5 <4.0	<2.3	<2.3
K₂O	0.80	0.39				•	
NA ₂ O	0.20	0.30	!				
Mn ₂ O ₃	0.50	0.05					
P ₂ O ₅	0.16	0.07					
TiO ₂	0.27	0.26					
CI	0.01	0.01					
Total	99.84	100.33					
Silica ratio	2.4	2.9					
Alumina ratio	2.4	0.9					
Lime saturation	99.6	93.4					
C₃S	59.9	65.1			<35		
C₂S	14.4	16.2			>40		
C₃A	11.7	2.8		<8	<15	<7	<5
C₄AF	7.6	12.7					<20 **

^{*} depending on C₃A content

It is obvious in Table 48 that mix I conforms to the specifications for type I (ordinary Portland cement) and type III (high early strength), but not for the other types.

Mix II conforms to all cement types except type IV (low heat of hydration).

If a composition of a potential raw mix does not meet the specifications for a particular type of cement, the following measures have to be weighed:

- Modification of proportioning criteria (lime saturation factor, silica ratio, C₃A- or Al₂O₃ content, etc.)
- Selection of necessary corrective materials (silica sand, etc.)
- Replacement of components (replacement of an alumina rich claystone by a silica-rich material for production of ASTM type IV and V cements, etc.)
- ◆ Replacement of the selected fuel type or fuel quality (coal with little ash instead of coal with a high ash content, if the coal ash composition becomes a critically influencing parameter, etc.)

^{**} C₄AF + 2 C₃A



Influence of minor ("deleterious") elements

The main influencing effect of the so-called deleterious constituents or elements on preparation and production is discussed in chapter 4.4.2. The following deals only with limits and effects of these constituents in the cement raw mix. Under normal circumstances, the following ranges and limits are to be expected:

Table 49 Deleterious constituents in cement raw mixes

deleterious constituents	"normal" range % (clinker basis)	limits % (clinker basis)	remarks
Alkalis:			
K₂0	0,5 - 0,8	0,6	for low-alkali
Na ₂ O	0,2 - 0,4	as Na₂O	clinker
MgO	1 - 3	5 - 6	according to local specifications
SO ₃	0,2 - 1,0	1 - 1,5	higher SO ₃ in clinker reduces quantity of gypsum to be added
P ₂ O ₅	0,0 0,3	0,5 - 0,8	
Cl	0,01 - 0,03 (0,01 - 0,1)		depending on and determining the process
F	0,01 - 0,1		air pollution
Cr₂O₃	0,01 - 0,04		dermatitis
Fe ₂ O ₃	3 - 5	0,3	for white cement production

These limits should not be regarded as isolated figures but rather as part of a multicomponent system (including contributions from the fuel). Particular attention should be given to the systems of:

whereby an effort should be made to achieve equalised alkali sulphur balance in order to prevent problems in the kiln system.

Only a few deleterious constituents are limited by specifications, e.g. the MgO and the total alkali-content (for low-alkali clinker). The others are not specified (limited) but practical experience with processing and quality requirements of the product (clinker/cement) dictate their quantitative limits.

4.3 <u>Assessment of the Mineralogical Composition of Cement Raw Mixes.</u>

A routinely performed assessment of a raw mix includes as a very important part the examination of the mineralogical composition (Table 50).



Table 50 Mineralogical assessment of raw mix

Minerals	Effects on technology
Aragonite (CaCO ₃)	dry grinding → coating in the mill and high power consumption
Quartz (SiO ₂)	grinding → abrasion, wear and high power consumption
	burning → impairs burnability
Feldspar	burning → impairs burnability, low reactivity
Clay minerals:	
Montmorillonite	preparation → water absorption,
Illite	stickiness
Kaolinite	burning $ ightarrow$ improved burnability
Chlorite	dust production $ ightarrow$ reduced dust prod.
Mica	coating properties → facilitates coating
Palygorskite	
Minerals of good crystallinity	reactivity low, require more energy for transformation
Minerals of low crystallinity	reactivity high, less energy necessary for transformation

4.4 <u>Assessment of Raw Mixes with regard to Cement Production and Choice of Process</u>

As discussed previously, the properties of the raw materials, i.e. raw mixes, largely influence the choice of process in general, and the various stages of production. Tables 51 and 52 indicate the most significant relations and functions.



Table 51 Significance of raw mix properties in cement production. (Compare also Table 51 p. 5/3 referring to raw material properties).

Aspects of production	Raw mix properties
Quarrying Crushing Transport Storage Grinding	see Table 40
Slurry preparation	clay mineral content, fineness
Drying	clay mineral content, porosity
Homogenising	chemical and mineralogical variability
Nodulising	clay mineral content
Dewatering	clay mineral, slurry characteristics(filtration)
Burnability	mineralogical composition, fineness, degree of weathering, intergrowth and size of rock fragments
Dust formation	mineralogical composition crystallinity
Coating formation	chemical composition

It becomes obvious that the clay mineral content is of paramount importance form many aspects of production.

Table 52 Summarises the most important raw mix properties influencing the choice of process.

Raw mix properties	Related features	WET PROCESS	DRY PROCESS
moisture content	clay mineral content, porosity	high	low
plasticity, stickiness	clay mineral content	high	low
homogeneity	chemical, physical and mineralogical variability	poor	high
chemical characteristics	chemical composition regarding alkalis, sulphur, chloride, etc. (contents)	high	low

Table 52 only summarises raw mix aspects. However, other factors, e.g.

- seasonal fluctuations of moisture content
- transport, haulage etc.

are, of course, also determining factors in the choice of process.

4.5 Evaluation of Laboratory Test Results

The steps which are regarded as the final part of a mix design, are preparation, examination and evaluation of test results produced in a laboratory.



4.5.1 Preparation

The proper preparation of laboratory raw mixes for testing is the prerequisite for reliable test results and subsequent evaluation.

It is as important as sampling and it should, therefore, be emphasised that both these processes have to be carried out under observation of strictly defined rules and controls.

4.5.2 Significance of Laboratory Investigations

The characteristics and behaviour of a cement raw material or mix during the various stages of production can never be predicted on the basis of the test results and findings of laboratory investigations alone. Laboratory testing has the disadvantage that many influencing and technologically important parameters such as kiln atmosphere, industrial preparation, etc., can be neither simulated nor reproduced on a laboratory scale. Laboratory produced test results, however, permit the recognition and interpretation of tendencies, whereby a broad variety of individual findings assures a more reliable final evaluation. It is thus recommendable to conduct a series of tests, the results of which can be used to support and control each individual finding. For instance, when the filtration properties of a cement slurry have to be assessed, mineralogical/chemical investigations grain size distribution tests, rheological tests on slurry and specific filtration tests should be conducted rather than a specific filtration test only. The same idea is applicable for all the other assessments of technological properties such as burnability characteristics, grindability properties, etc.

In order to guarantee that the laboratory results correspond as closely as possible to the findings of industrial practice, the design of the laboratory testing methods and other aspects such as limits, reproducibility, etc. should periodically be checked and compared.

4.5.3 Summary of Laboratory Tests

The following tests are available and normally applied in the cement industry (Table 53).

Table 53 Laboratory tests

Material aspects	Test designation	Limits, reproducibility, practice relevance
Stickiness	soil tests	
Burnability	burnability test	tendencies only, but good practice relevance
Grindability	grindability test	quantitative estimate of kWh/t requirements
Volatility of circulating elements	volatility test	quantitative estimate of primary volatility in various atmospheres
Coating behaviour brick selection	coating test	tendencies only, acceptable practice relevance
Filterability	filtration test, testing of slurry rheology	quantitative estimate of key-factors quantitative assessment of rheology
Nodulisability	granulation test, thermo-shock test strength test	tendencies only, practice relevance acceptable

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Normally these technological tests are supported by:

- chemical analysis (highly accurate)
- mineralogical analysis (semi-quantitative)
- grain-size analysis (accurate)